

## NEW WETTING AND DISPERSING ADDITIVES FOR SOLVENT BORN GRAVURE INKS

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### ABSTRACT

Synthesis of some non-ionic wetting and dispersant additives based on polyethylene glycol of M.wt 1000 g/mol as hydrophilic segment with different hydrophobic segment saturated fatty acids such as Lauric, Myristic, Palmitic and Stearic acids as surface active di-block wetting and dispersing agents. Effect of different types of fatty acids on gloss, transparency and viscosity of prepared gravure inks made from Yellow C.I 13, Red C.I 57:1, Blue C.I 15:4 and Black C.I 7 were studied. The FTIR and <sup>1</sup>H NMR were studied to confirm the structure of synthesized samples

**Keywords:** wetting and dispersing agent – gravure printing inks.

### INTRODUCTION

Gravure printing inks is very important industry as feed stock for printing of flexible packaging and its quality is significant affect by additives used in formula, especially wetting and dispersing agent which overcomes on aggregates and agglomerates of pigments which take places during storage and transport.

In an ink formulation, the pigment must be dispersed and stabilized to achieve good color strength, gloss and transparency. Stable, concentrated dispersions with small particles and narrow particle size distribution potentially can lead to higher gloss and color strength per unit mass of pigment.

Polymeric hyperdispersants have been adopted by the manufacturers of surface coatings for a variety of reasons, all generally associated with improvements in the state of pigment dispersion.<sup>1</sup> The benefits can be split into three basic categories:

1. High productivity through dispersions of high pigment loading without increasing of viscosity.
2. Reduction in mill time during the manufacturing of mill bases which can be letdown into a varieties of base paints.
3. Improving the quality, particularly:
  - Better coating properties, especially flow and gloss.

- Superior color development as show in Figure 1.
- Enhanced flocculation resistance.
- Improved color stability.

Polymeric hyperdispersants can be simplistically described as having two key components in their structure, anchoring groups that adsorb on to the pigment surface and polymeric chains that provide the steric stabilization barrier around the pigment particle. Pigment dispersants for use in organic solvent systems are polymeric and may be either random or structured copolymers.

Because of minimum dispersion viscosity is achieved with structured dispersants, these materials have become more important in the race to reduce solvent emissions.

Saturated fatty acids series esterified with polyethylene glycol of M.wt 1000 g/mol as diblock polymer dispersants explored in this work.

Polymeric pigment dispersants were discussed by Schofield<sup>2</sup>. Pigment dispersions are thought to work by forming a layer around the pigment which extends into the surrounding medium to provide entropic stabilization. In order for the pigment particles to come close enough to one another to flocculate, the stabilizing layer on one pigment particle must be forced into the layer on another. This causes an increase in concentration within the area between the

pigment particles, and this ordering is counter to the entropic tendency in nature to disorder. Further reference to this theory can be found in Reference<sup>3</sup>. Charge and steric or entropic stabilization is shown in Figure 2. Jakubauskas has investigated the relative effectiveness of random and structured copolymers as dispersants and indicates that comb and block configurations are equally effective for dispersing pigments, and more effective than random copolymers which can cause the viscosity to increase upon storage by bridging between pigment particles<sup>4</sup>.

Hutchins and Shor described methacrylate AB block copolymer dispersants<sup>5</sup>.

Soluble polymers can act as dispersants by adsorption of some segments, while other segments form solvated loops and tails. Copolymers are preferred since they can contain less well solvated segments which are better anchors. This is especially true when all the insoluble segments are linked to form a large block<sup>6</sup>. Classical dispersants such as linear (co)polymers of acrylic- or maleic acid were and still are used in many applications<sup>7</sup>. Generally result in a poor dispersion stability. Improvements in dispersion stability have been obtained using block copolymer dispersants<sup>8</sup>. AB dispersants are known having typically a polar group known as the A segment on one end to facilitate attachment to a pigment surface, and a non-polar oligomeric group known as the B segment on the other end to enhance steric stabilization of the pigment particle in a dispersion<sup>9</sup>. The condensation products of fatty acids with polyethylene glycols comprise monoesters and esterification is a state of equilibrium where water must be removed as soon as it is formed. This can be done (Abd Hamid 2004) by carrying out the process at temperatures above 100°C and/or in the presence of a proper acidic catalyst or an Azeotrop in an isotropic distillation.

Preparation and emulsifying properties of polyethylene glycol (1500) diesters of fatty acids was discussed by D.N BHATTACHARYYA<sup>10</sup>. Preparation and surface active properties of polyethylene glycol (600) monoesters of fatty acids was achieved<sup>11</sup>. Polyethylene glycol (PEG) monoesters of fatty acids, being low foamers and good emulsifiers, find extensive use in textile industry and pesticide formulations and also in cosmetic preparations<sup>12</sup>. PEG fatty acid esters are prepared by either ethoxylation<sup>13&14</sup> or esterification<sup>15</sup>.

The latter process is safer and easily controllable as desired. Even here, considerable proportions of diesters are formed unless a large excess of glycol is employed<sup>16</sup>.

Pure monoester can be readily obtained by forming a borate with glycol then esterifying with a fatty acid<sup>17</sup>. This route had been applied earlier for the preparation of varieties of monoesters of ethylene glycol as intermediates for pure mixed diesters<sup>18</sup>.

In accordance with this article there are provided procedures for the preparation of non-ionic pigment dispersants by esterifying lauric, Myristic, Palmitic and stearic acid with Polyethylene glycol (1000) alternatively as non-ionic organic pigment dispersants for gravure printing inks.

Preparation of series of organic pigment dispersants are efficient and cheaper than other commercial grades such as Solsperse® 20000 to replace it in the Egyptian market as inexpensive wetting and dispersing agent.

## EXPERIMENTAL

### 2.1. MATERIALS

Polyethylene glycol (1000) was supplied from CarlRoth, (Germany), Lauric, myristic, palmitic and stearic acid were supplied from Aldrich Chemical Company (USA), Titanium(IV) n-Butoxide catalyst was supplied from Drof Katel company (India), Pigment yellow C.I 13, Pigment red C.I 57:1 were supplied from Hangzhou pigment Company (China), Pigment blue C.I 15:4 was supplied from Ramadev Company (India), carbon black was supplied from Spring Green (China).,

Nitrocellulose 18-25 BN was supplied from Nitro Quimica Company (Brazil), Solsperse® 20000 was supplied from Lubrizol Company (England), Ketonic resin was supplied from DR Coat (India), Acetyl tributyl citrate was supplied from Egy Polymers Company (Egypt), Ethylacetate, Ethanol and Methoxy propanol supplied from Sasol (South Africa), Glass beads mills 0.3 and BOPP film were supplied from PAN Egypt Company (Egypt).

And all chemicals and materials were used without further purification.

### 2.2. DISPERSING AGENT PREPARATION

#### 2.2.1. GENERAL PROCEDURE FOR THE SYNTHESIS OF DISPERSANT

The reaction was carried out in a 500ml round glass flask equipped with Dean and Stark apparatus with porcelain balls (2ml in diameter) as stirrer. Heating was conducted in a thermostatic oil bath. 0.2 mole of dried fatty acid to 0.22 PEG was melted at 70°C and thoroughly mixed with a specific amount of titanium (IV) n-butoxide. Then, Dean and Stark apparatus was fitted onto the flask in an oil bath. The temperature raised from 70°C to 180°C, where the reaction held for 12 hrs then the flask was taken out of the bat and cooled at room temperature then samples were

discharged for purification, analysis and application.

### 2.2.2. PRODUCT PURIFICATION

The mixture of esters was separated from the unreacted fatty acid and PEG by dissolving the samples in ethyl acetate at a liquid / product ratio of 10:1 at  $35 \pm 1^\circ\text{C}$ , and transferred to a separating funnel (about 3 times the volume of the ethyl acetate solution).

5 successive washings were given to the ester solution, each with an equivolume amount of the aqueous solution containing NaCl (30 weight percent) and NaOH (2 weight percent to remove the fatty acid and catalyst), followed by 5 successive washings, each of equivolume amount, to remove salinity and remnant alkalinity. The ethyl acetate layer was then evaporated in a rotavapour at  $80^\circ\text{C}$  in a vacuum until dryness to get the mixture of esters<sup>19</sup>.

### 2.3. THE CHARACTERIZATION TECHNIQUE OF THE PREPARED DISPERSANTS.

Nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on Jeol ECA-500 run at 500 MHz. The polyester samples were dissolved in  $\text{CDCl}_3$ , and tetramethylsilane was used as the reference standard.

Infrared spectroscopy (FTIR) the FTIR spectra of polymers were recorded by JASCO FTIR 6100 in the range of  $4000\text{--}400\text{ cm}^{-1}$  using KBr pellets.

#### 2.3.1 ( $^1\text{H}$ NMR) OF THE PREPARED DISPERSANTS

Figure (4-5) shows  $^1\text{H}$ NMR of the prepared block copolymer. The protons of the fatty acid segments of the dispersant could be assigned as follow, four protons of Fatty acid moiety (a Fig 4) at ppm 0.82, four protons of PEG (b Fig 4) at ppm 2.4 and four terminal protons of polyethylene glycol (e, f Fig 4) at ppm 3.6 and 4.3.

#### 2.3.2 (FTIR) OF SYNTHESIZED DISPERSANTS

The FTIR of the prepared dispersants with PEG (1000) are shown in figure 3. The characteristic bands could be assigned as follow; C=O stretching band of the ester group occurs at  $1737\text{ cm}^{-1}$ , C-O stretching band occurs at  $1170\text{ cm}^{-1}$ , C-H stretching occurs at  $2880\text{ cm}^{-1}$ ,  $2956\text{ cm}^{-1}$  (symmetrical and asymmetrical respectively),  $\text{CH}_2$  bending occurs at  $1463\text{ cm}^{-1}$  and OH stretching band at  $3458\text{ cm}^{-1}$ . The IR charts for dispersants with different saturated fatty acids shown in figure 6. There is no difference in the peak assignment of the all dispersants.

### 2.4. EVALUATION OF THE PREPARED PRODUCTS AS PIGMENT DISPERSANTS PRINTING INK PREPARATION

Synthesized polymeric dispersants were tested in gravure printing inks formulations. dispersant in printing inks formula disperse pigment aggregation and agglomeration to achieve the desired properties such as gloss, color strength, transparency and viscosity.

All synthesized dispersants were used in table 1 formulations using different organic pigments such as yellow C.I 13, process Red C.I 57:1, process Blue C.I 15:4 and carbon black C.I 7 to evaluate it against Solsperser® 20000 & blank sample.

The inks were dispersed with glass beads of 1mm diameter by using Red-Devil shaker for 60 minutes.

*\*every synthesized dispersant (PEG1000-L – PEG1000 M – PEG1000-P – PEG1000-S), blank sample and Solsperser® 20000 were tested with all pigments in the above formula.*

#### DRY GLOSS MEASUREMENT (ASTM D523)

The gloss degree was measured by Minigloss which is a gloss meter from Sheen Instruments Company has a measuring geometry 60 Degrees, resolution 0.1 gloss unit and accuracy

$\pm 1.0$  gloss unit (against reference standard).

#### SPECTRODENSITOMETER (ASTM D7305-08)

The Color hue, color strength and transparency were measured by X-rite 504 (spectrodensitometer) from X-rite company has a measuring geometry 45%, Spot Size at Sample 3.4mm (0.13 inch) standard and measurement range 0.00 D – 2.5 D; 0 – 160 % R with measurement time approx. 1.4 seconds, approx..9 seconds for consecutive measurements in speed read mode and repeatability  $\pm 0.005\text{D}$ .

#### VISCOSITY MEASUREMENT (ASTM D1200)

The viscosity was measured by ford cup#4 (cup viscometer) from BYK-Gardner GmbH. It has efflux time 20 - 105 and orifice diameter 0.16 inch.

#### DRAWDOWNS APPLIED BY HAND COATER BAR

The drawdowns of ink samples were tested at delivery viscosity on corona treated transparent BOPP film by using rubber bed and wire hand coater No. 1 (6 microns).

### 2.4.1 GLOSS MEASUREMENT

The gloss is the surface property which describes it as shiny or lustrous, metallic or matte. The gloss values of printed films indicate directly the performance of synthesized non-ionic organic pigment dispersants, as it reflects the mechanism of action to disperse aggregates and agglomerates of pigment particles.

In general, the gloss of all pigmented systems, is affected by a higher or lower extent of the pigment size and distribution of the pigment particles during its dispersion. Surface-treated pigments with dispersants are more easily dispersible, leading to more stable dispersions in fluid media with improved gloss of the printed films, when compared with untreated pigments.

All data concerning the gloss of printed films are shown in table 2.

#### 2.4.1.1 GRAVURE INK OF YELLOW PIGMENT C.I 13

Inks prepared from PEG1000-M showed a close results against Solsperser® 20000, while PEG1000-L, PEG1000P and PEG1000-S were less than standard as in Figure 7.

#### 2.4.1.2 GRAVURE INK OF RED PIGMENT C.I 57:1

Inks prepared from all synthesized organic dispersants showed better gloss than inks prepared with Solsperser® 20000, especially PEG1000-S as in Figure 8.

#### 2.4.1.3 GRAVURE INK OF BLUE PIGMENT C.I 15:4

Inks prepared from all synthesized organic dispersants showed better gloss than inks prepared with Solsperser® 20000, and the best result for PEG1000-L then PEG1000-M as in Figure 9.

#### 2.4.1.4 GRAVURE INK OF BLACK PIGMENT C.I 7

Inks prepared from all synthesized organic dispersants showed better gloss than inks prepared with Solsperser® 20000, but the best result of PEG1000-L then PEG1000-M as shown in Figure 10.

### 2.4.2. TRANSPERENCY MEASUREMENT

It is usually determined by applying the pigmented system to a black back-ground which its darkness is retained or reduced according to the transparency of the layer. Scattering increases the opacity of a layer, while the light transmitted increases by more transparent pigments. The transparency values indicate the dispersion quality and related to the dispersant selection.

The transparency data of prepared pigmented ink were recorded as in table 3.

#### 2.4.2.1. GRAVURE INK OF YELLOW PIGMENT C.I 13

Transparency of Solsperser® 20000 was better than all synthesized dispersants, but the closest one was PEG1000-M as shown in Figure 11.

#### 2.4.2.2. GRAVURE INK OF RED PIGMENT C.I 57:1

The best results were recorded for PEG1000-S and PEG1000-L, meanwhile PEG1000-M and PEG1000-P are still better than Solsperser® 20000 as in Figure 12.

#### 2.4.2.3. GRAVURE INK OF BLUE PIGMENT C.I 15:4

All synthesized dispersants were better than Solsperser® 20000, and the best result was recorded for PEG1000-L as shown in Figure 13.

### 2.4.3. VISCOSITY MEASUREMENT

Viscosity is the resistance to flow and the most important rheological characteristic of liquids and therefore of coatings and inks. Even more significant is the way in which viscosity changes during coating and printing. Newtonian fluids, like solvents, have an absolute viscosity that is unaltered by the application of mechanical shear. However, virtually all coatings show a significant change in viscosity<sup>(11)</sup>. The dispersants play important role to achieve low viscosity of dispersion medium during grinding stage and allow the formulator to make high pigment volume concentration without thixotropic phenomena which lead to save process, time and cost. The viscosity values of prepared pigmented ink were recorded as in table 4.

#### 2.4.3.1. GRAVURE INK OF YELLOW PIGMENT C.I 13

All synthesized dispersants recorded lower viscosities than Solsperser® 20000, especially PEG1000-S and PEG1000-P as shown in Figure 14.

#### 2.4.3.2. GRAVURE INK OF RED PIGMENT C.I 57:1

PEG1000-L, PEG1000-M and PEG1000-P recorded less viscosities than Solsperser® 20000, except PEG1000-S which increases the viscosity as shown in Figure 15.

### 2.4.3.3. GRAVURE INK OF BLUE PIGMENT C.I 15:4

All synthesized dispersants recorded higher viscosities than Solsperser® 20000, as shown in Figure 16, which indicates the lower efficiency of these dispersants against Solsperser® 20000.

### 2.4.3.4. GRAVURE INK OF BLACK PIGMENT C.I 7

PEG1000-L, PEG1000-M, PEG1000-P and PEG1000-S recorded higher viscosities than Solsperser® 20000 as show in Figure 17.

## 3. CONCLUSION

PEG (1000) is condensed with different saturated fatty acids of Lauric, Myristic, Palmitic and Stearic acids via esterification

technique in presence of titanium(IV) n-butoxide as Catalyst.

The structure of the prepared wetting and dispersing agent was confirmed by IR and  $^1\text{H}$ NMR.

The gloss, transparency and viscosity of prepared gravure inks of different organic pigments such as Yellow C.I 13, Red C.I 57:1, Blue C.I 15:4 and Carbon black C.I were measured and its performances were characterized against Solsperser® 20000.

Most of synthesized dispersants showed an excellent gloss, transparency and viscosity which reflect its efficiencies as new wetting and dispersing agents for gravure inks to replace Solsperser® 20000 with lower cost and simple technique.

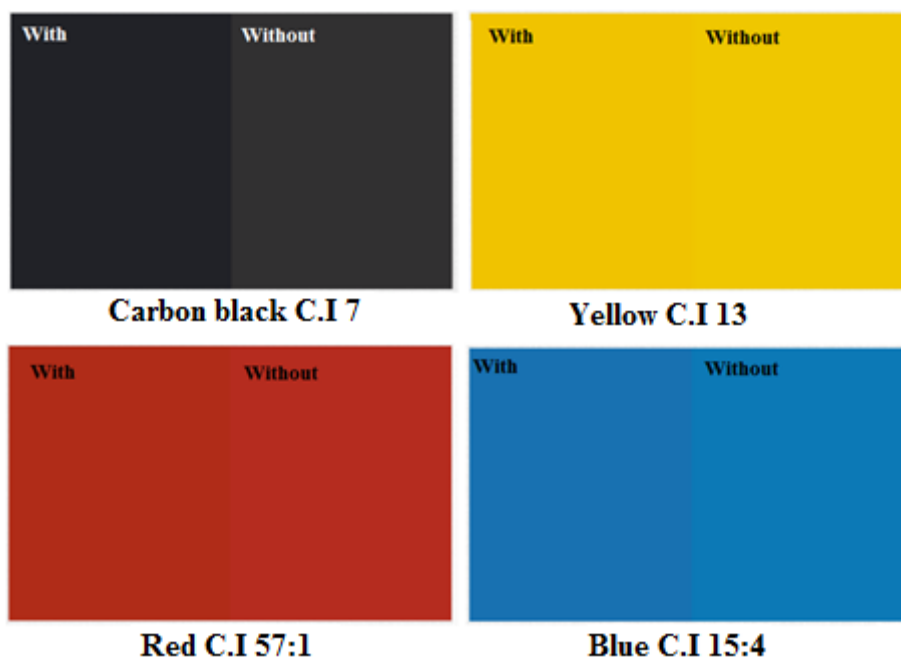


Fig. 1: Effect of wetting and dispersing agent on different organic pigments

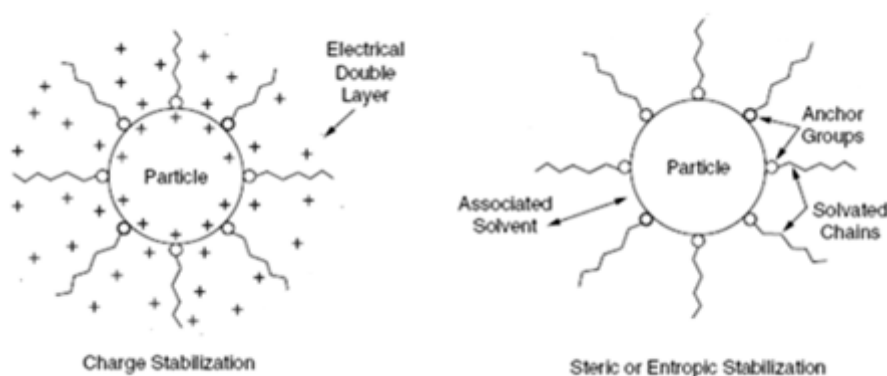
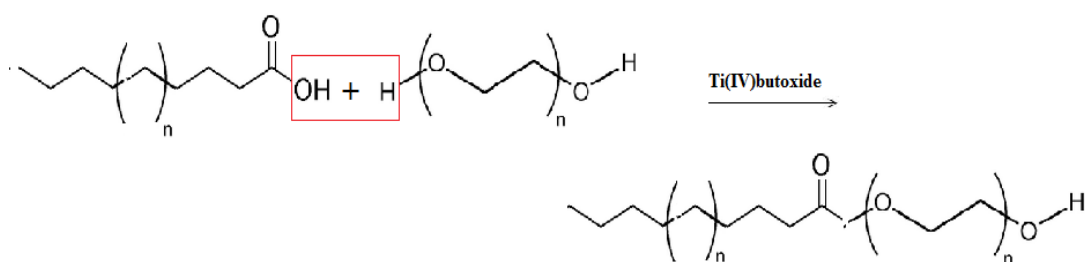
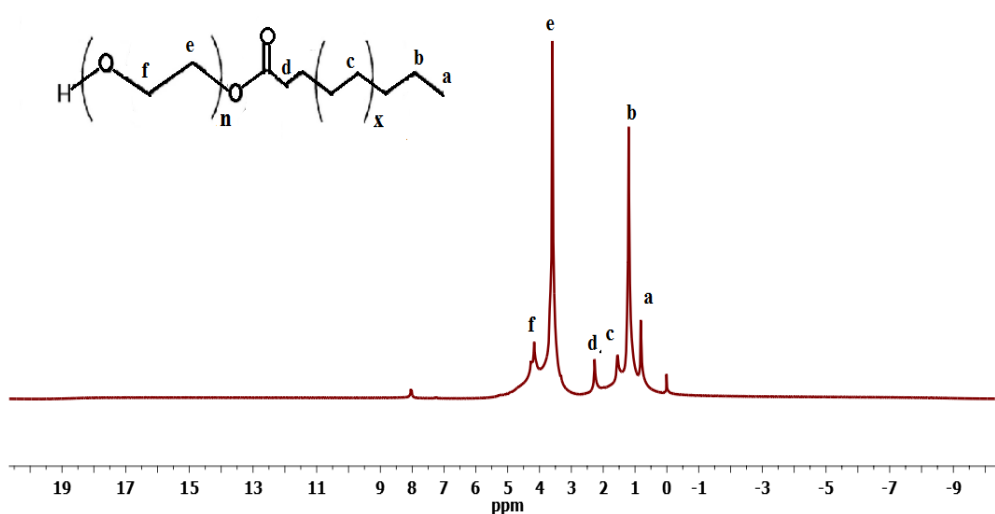


Fig. 2: Charge and steric or entropic stabilization

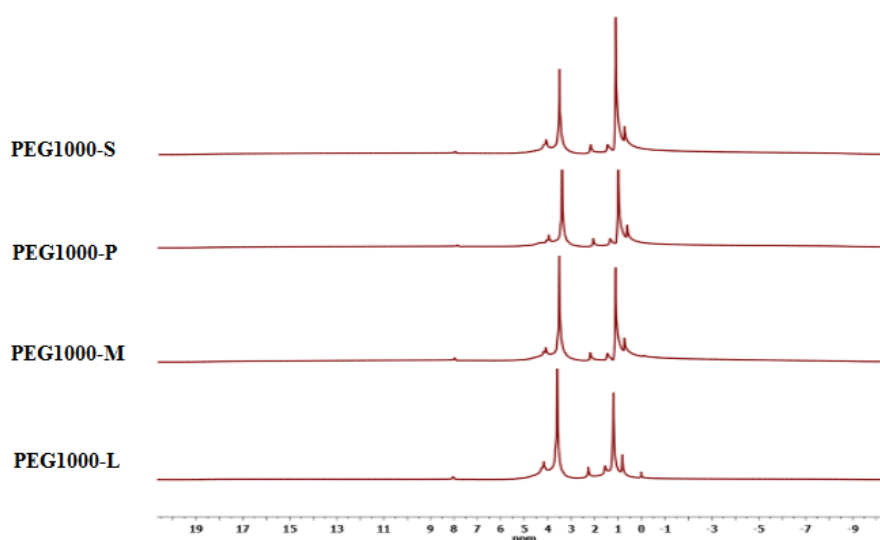


**Fig. 3: Synthesis of fatty acid with polyethylene glycol in presence of titanium (IV) n-butoxide as homogenous catalyst**



**Fig. 4: Show <sup>1</sup>H NMR of PEG1000-L**

By the same way, the structure of all block copolymers were elucidated and represented in Figure 4.



**Fig. 5: <sup>1</sup>H NMR of PEG1000-L, PEG1000-M, PEG1000-P & PEG1000-S**



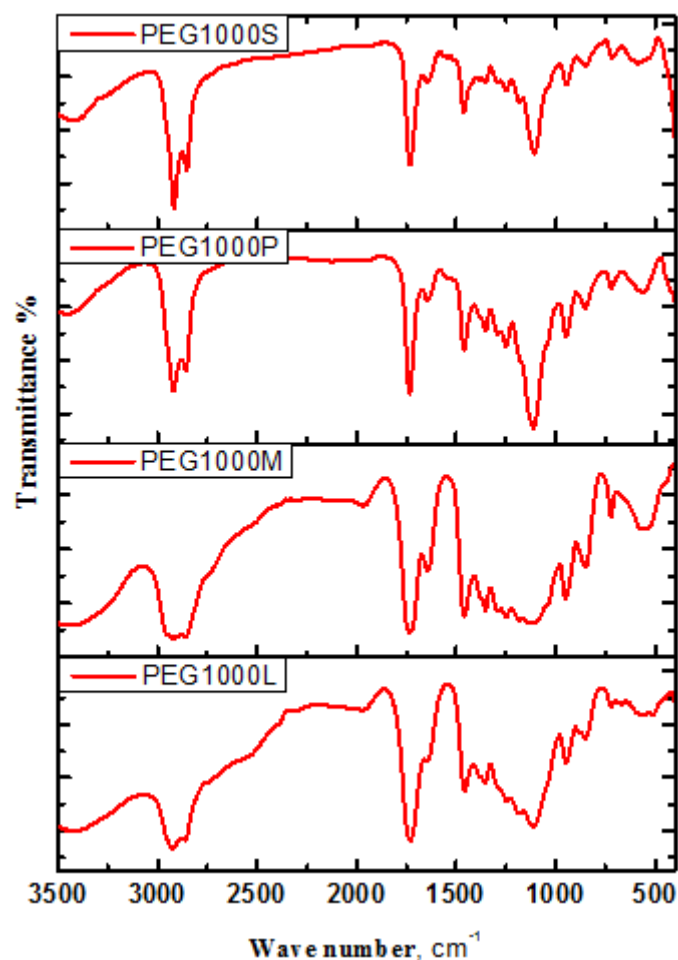


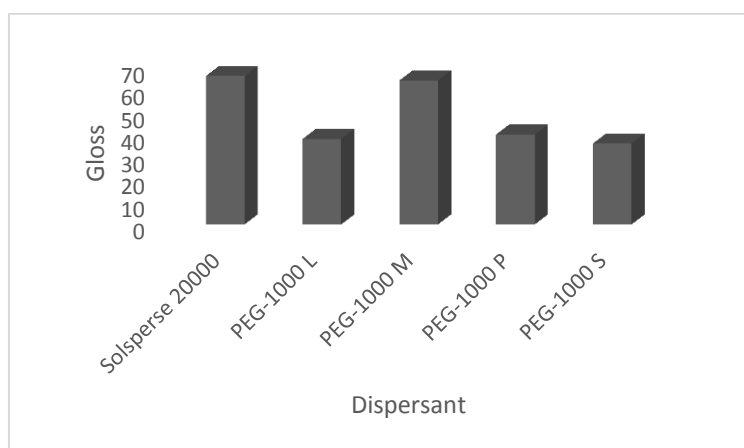
Fig. 6: Shows IR for all prepared polymers

Table 1: Liquid printing inks formulations prepared by different dispersants

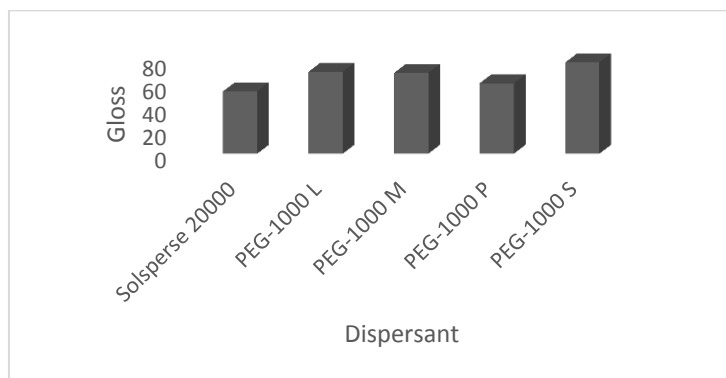
Material	Cyan	Yellow	Magenta	Black
Pigment Cyan C.I 15:4	12	---	---	---
Pigment Yellow C.I 13	---	9	---	---
Pigment Magenta C.I 57:1	---	---	11	---
Pigment Black C.I 7	---	---	---	12
Dispersing agent*	2	1	1	3
Nitrocellulose 1/8 S	19	16	18	18
Ketonic resin	3	3	3	3
Acetyl tributyl citrate	4	4	4	4
Ethanol	10	30	10	10
Ethyl acetate	50	37	53	50

Table 2: Gloss of printed films of different inks by using variety of pigments and synthesized dispersants against commercial and blank samples

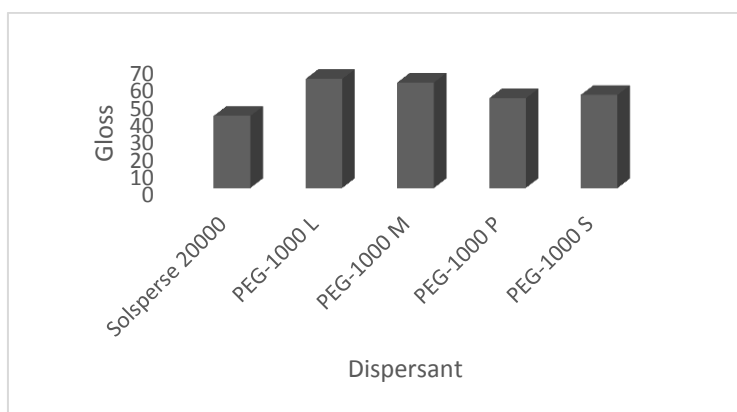
No.	Dispersant	Yellow	Magenta	Cyan	Black
1	Solsperse® 20000	66	54	41	60
2	PEG1000-L	38	71	62	35
3	PEG1000-M	64	70	60	38
4	PEG1000-P	40	61	51	42
5	PEG1000-S	36	79	53	42



**Fig. 7: Gloss of yellow gravure ink prepared by synthesized dispersants**

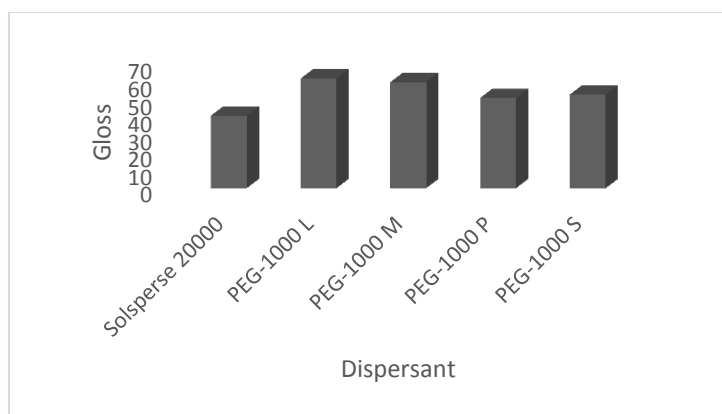


**Fig. 8: Gloss of Red gravure ink prepared by synthesized dispersants**



**Fig. 9: Gloss of Blue gravure ink were prepared by synthesized dispersants**

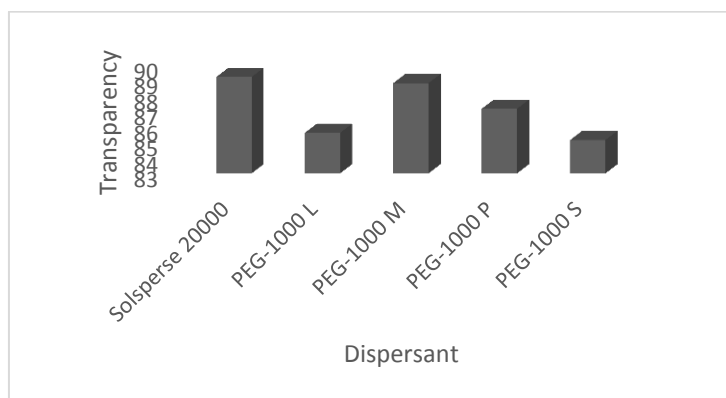




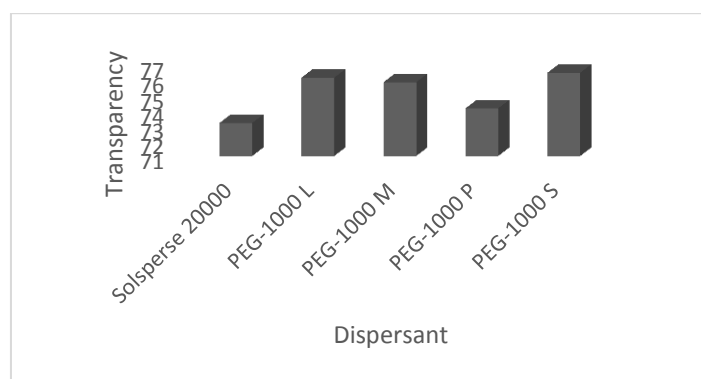
**Fig. 10: Gloss of Blue gravure ink prepared by synthesized dispersants**

**Table 3: Transparency of printed films with different pigmented inks by using synthesized dispersants against Solsperse® 20000 and blank samples**

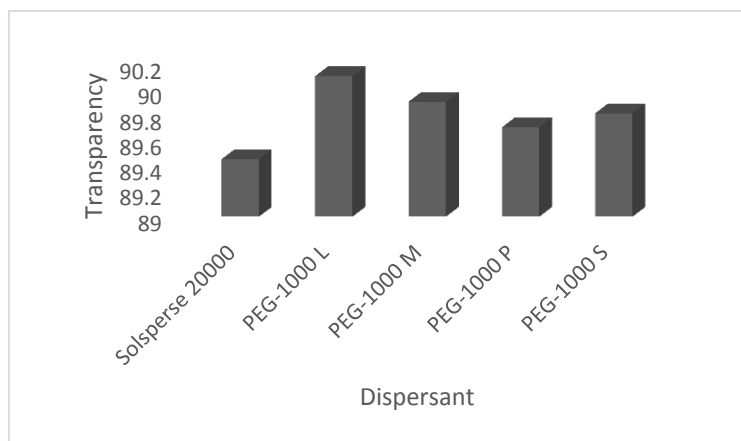
No.	Dispersant	Yellow	Magenta	Cyan	Black
1	Solsperse® 20000	89.12	73.15	89.45	NA
2	PEG1000-L	85.57	76.10	90.10	NA
3	PEG1000-M	88.73	75.80	89.90	NA
4	PEG1000-P	87.10	74.10	89.70	NA
5	PEG1000-S	85.12	76.42	89.81	NA



**Fig. 11: Transparency of Yellow gravure ink were prepared by synthesized dispersants**



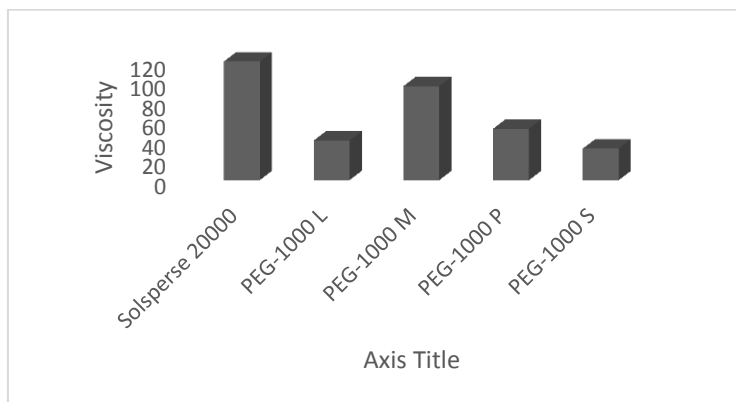
**Fig. 12: Transparency of Red gravure ink prepared by synthesized dispersants**



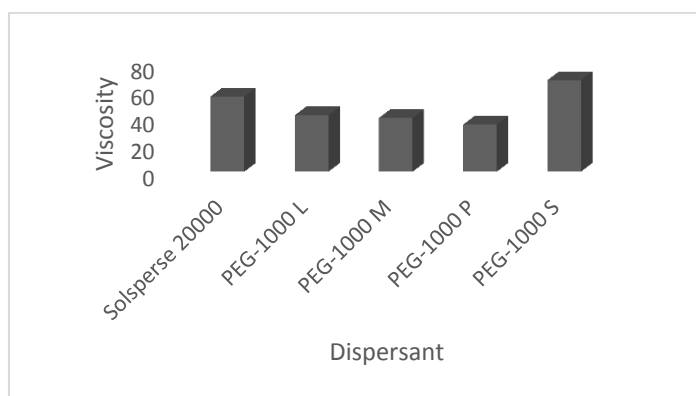
**Fig. 13: Transparency of blue gravure ink prepared by synthesized dispersants**

**Table 4: Viscosity of different pigmented liquid inks prepared by using synthesized dispersants against Solsperser® 20000 and blank samples**

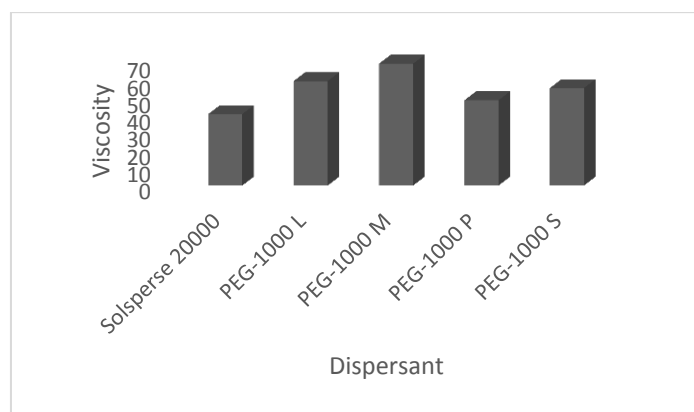
No	Dispersant	Yellow	Magenta	Cyan	Black
1	Solsperser® 20000	120	56	41	45
3	PEG1000-L	40	42	60	65
4	PEG1000-M	95	40	70	67
5	PEG1000-P	52	35	49	60
6	PEG1000-S	32	68	56	62



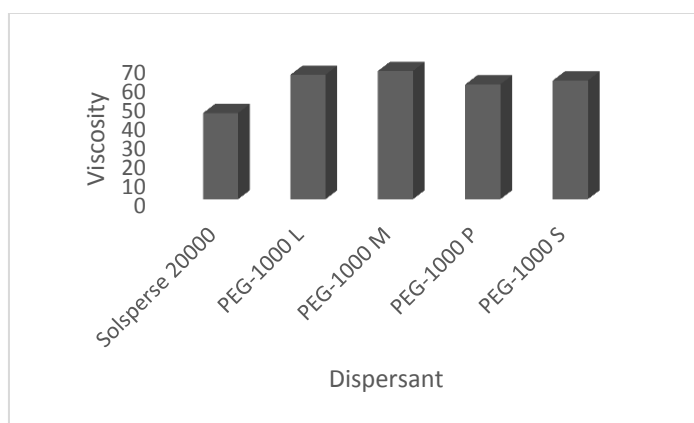
**Fig. 14: Viscosity of gravure yellow ink prepared by synthesized dispersants**



**Fig. 15: Viscosity of gravure red ink prepared by synthesized dispersants.**



**Fig.16: Viscosity of gravure blue ink prepared by synthesized dispersants**



**Fig. 17: Viscosity of gravure black ink prepared by synthesized dispersants**

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